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BIOPHYSICS OF INERT GASES RELATED TO DIVING(U) MICHIGAN  
STATE UNIV EAST LANSING DEPT OF PHYSICS AND ASTRONOMY  
G L POLLACK MAY 82 N00014-80-C-0617

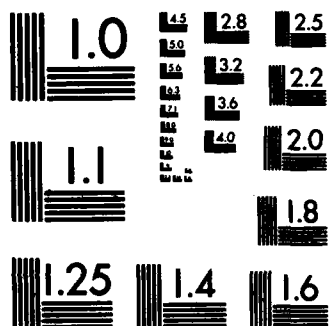
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Title: Biophysics of Inert Gases Related to Diving

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The work done under this contract is described below under two headings: A. Solubility of Inert Gases in Liquids, and B. Diffusion of Inert Gases in Liquids. Section C is a list of papers which have been published from research under this contract and Section D is a list of abstracts and presented papers.

A. Solubility of Inert Gases in Liquids

→ One of the main aims of this research is to understand from first principles what determines the solubility of a gas in a liquid. In order to make this general and difficult problem more tractable, we initially limited our experiments to <sup>STUDIED</sup> studying the solubility of the inert gas Xe in simple liquids. Our plan is to pursue an ordered series of experiments from simple systems to complex systems, deepening our understanding as we proceed.

→ One of the first experimental systems studied was Xe gas in water-sucrose solutions. The work is described in Reference 1 of C in detail; a brief discussion appears in B.

→ The principal system which we studied, and are still studying, is the solubility of Xe gas in normal-alkanes. → In the initial experiments (Reference 2 of C) we measured the Ostwald solubility (L) of  $^{133}\text{Xe}$  at  $20.0^\circ\text{C}$  in n-alkanes from  $n\text{-C}_5\text{H}_{12}$  (for which  $L = 5.39$ ) to  $n\text{-C}_{16}\text{H}_{34}$  (for which  $L = 3.14$ ). The idea behind choosing this system is that the n-

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alkanes form a homologous series of nonpolar organic liquids whose properties change in an ordered way as the number of C-atoms in the molecules increases and as the temperature changes. They are in some sense the simplest organic liquids.

The motivation for choosing Xe is that it is an inert gas whose interactions with nonpolar molecules are mainly Van der Waals interactions. Such interactions are weak and short-range and relatively well understood. This gas has a radioisotope,  $^{133}\text{Xe}$ , which is well suited for laboratory studies. Xe-133 is a product of fission of  $^{235}\text{U}$  and is readily available commercially; it decays with a half-life of about five and a quarter days and it emits a gamma ray of energy 81 keV which can be conveniently observed. We have in the course of this research developed methods for measuring the specific radioactive intensity of  $^{133}\text{Xe}$  gas and from this we determine the concentration of Xe. The technique is accurate and versatile. It can be straightforwardly extended to radioactive isotopes of other gases and in future we propose to study solubility of other gases using it.

For the experiments described in Ref. 2, we used these techniques to determine  $L(20.0^\circ\text{C})$ . From the Ostwald solubility one can determine the quantity  $x_2$ , i.e. the equilibrium mole fraction of solute gas in the solvent at a partial solute gas pressure of 1 atm. The relation connecting  $L$  with  $x_2$  is given as Eq. (2) of Ref. 2. The key connection between thermodynamics and solubility is through the Gibbs energy, also called chemical potential,  $\Delta\mu_2^0$ . This quantity is the difference in chemical potential associated with putting one mole of Xe gas into the liquid solution. It is determined from the solubility by:

$$\Delta\mu_2^0 = -RT \ln x_2 \quad \text{Eq. (1).}$$

Reference 2 presents data on  $L$ ,  $x_2$ , and  $\Delta\mu_2^0$  for the system  $^{133}\text{Xe} \rightarrow n\text{-alkanes}$ . It is fair to say that this is the most complete study of this system to date.

Figure 3 of Ref. 2 is a plot of the Gibbs energy versus the number ( $n$ ) of carbon

atoms in the alkane solvent molecule. The data fall remarkably close to the straight line:  $\Delta\mu_2^0 = -19.86 n + 2234$  cal/mole. This means that there is a decrease of 19.9 cal/mole for each C added to the chain. This relation is remarkably simple and gives support to the idea that the system under study is an excellent choice as a prototype for solubility studies. For this reason we studied the system further.

Starting in January of 1981 we supported under this contract as a research assistant Mr. Jeffrey F. Himm, a graduate student in the Department of Physics and Astronomy. The principal investigator and Mr. Himm have extended widely the measurements on the system Xe + n-alkanes. During this time we: (a) Measured the temperature dependence of  $L(T)$  over the range 10.0°C to 50.0°C, (b) Measured  $L(T)$  for n-alkanes from n-pentane ( $n\text{-C}_5\text{H}_{12}$ ) through n-eicosane ( $n\text{-C}_{20}\text{H}_{42}$ ), (c) Obtained from these results the enthalpy and the entropy of solution, and (d) Developed physical models with which the results can be partly understood.

A paper describing these results has recently been published in the Journal of Chemical Physics (Reference 3 in C below). We now describe some highlights of this research.

Figure 6 of Ref. 3 is a plot of the Gibbs energy of solution  $\Delta\mu_2^0$  in cal/mole as ordinate versus the number of C atoms per solvent molecule as abscissa. The results are shown there for all of the sixteen alkanes for which we took data (from  $n = 5$  to 20) and at all the temperatures at which we took data (10.0°C through 50.0°C at intervals of 10.0°C). These results come directly from the experimentally observable quantities by use of Eq. (1).

The most interesting feature of these data is their regularity. It is clear from Figure 6 that at each T the data are a linear function of n. The data are remarkable since they are simple functions of n as well as of T. In fact all of the data we have obtained in these experiments may be expressed with the empirical equation:

$$-RT \ln x_2 = \Delta \mu_2^0 = -0.0637nT + 2.575 \times 10^{-2} T^2 \quad \text{Eq. (2).}$$

Equation (2) fits all the data to better than 1%. As discussed earlier we chose the Xe  $\rightarrow$  n-alkane system because we expected it to be a simple well-ordered system. However the accuracy and universality of Eq. (2) are much better than expected and may even be unprecedented in this field. We plan to understand this equation and this system as well as possible.

Our main motivation in measuring the temperature dependence of solubility in the Xe  $\rightarrow$  n-alkane system was to obtain the two important thermodynamic quantities: (1) enthalpy of solution ( $\Delta \bar{H}_2^0$ ) and (2) entropy of solution ( $\Delta \bar{S}_2^0$ ). Although the chemical potential directly determines the solubility, it is itself a difficult thermodynamic quantity to understand since it has both an enthalpic contribution,  $\Delta \bar{H}_2^0$ , and an entropic contribution,  $-T\Delta \bar{S}_2^0$ . In general the chemical potential is:

$$\Delta \mu_2^0 = \Delta \bar{H}_2^0 - T\Delta \bar{S}_2^0 \quad \text{Eq. (3).}$$

What we have done in these experiments is to extract from our temperature dependent  $\Delta \mu_2^0(T)$  data the separate contributions of enthalpy and entropy. The importance of this is that these quantities can be separately related to relatively well understood physical ideas. For example,  $\Delta \bar{H}_2^0$  is closely related to the work required to bring one mole of Xe molecules from the vapor into the dilute solvent solution.  $\Delta \bar{S}_2^0$  is related to the difference in volume available for motion of the solute atoms in going from the vapor into the solvent. From our data we have been able to understand, to a certain extent quantitatively, the enthalpy of solution in these systems. This is illustrated in Figure 5 of Reference 3.

Figure 5 is a plot of three quantities on the ordinate axis versus the number of C atoms in the solvent molecule, on the abscissa axis. The filled-in dots are the negative of

the enthalpy of solution in cal/mole as determined in these experiments. The x's are the surface energies required to make enough spherical bubbles in the liquid, each of radius  $r_{\text{Xe}} = 2.23 \text{ \AA}$ , to accomodate one mole of Xe atoms. These quantities are taken to be equal to  $4\pi r_{\text{Xe}}^2 \gamma_{20^\circ\text{C}} N_A$  (cal/mole), where  $N_A$  is Avogadro's number and  $\gamma_{20^\circ\text{C}}$  is the surface tension of the solvent at  $20^\circ\text{C}$ .

We now assume that  $\Delta \bar{H}_2^0$  is the work required to bring  $N_A$  molecules of Xe into the solvent. We further assume that this work is the difference between the energy required to make spherical bubbles and the binding energy  $E_b$  between the Xe molecules and the alkane molecules. This gives the equation:

$$\Delta \bar{H}_2^0 = 4\pi r_{\text{Xe}}^2 \gamma_{20^\circ\text{C}} N_A - E_b \quad \text{Eq. (4)}$$

Finally the third set of points plotted on Figure 5 are values of  $E_b$  calculated from  $4\pi r_{\text{Xe}}^2 \gamma_{20^\circ\text{C}} N_A - \Delta \bar{H}_2^0 = E_b$ ; these are the open circles. If the Xe--n-alkane interaction is as simple as we have proposed, then the binding energy should be the same for Xe to all of the alkane molecules. What Figure 5 shows is that, to within the approximations of this model,  $E_b \approx 4500 \pm 140$  cal/mole, i.e. it is constant to about 3%. The dashed line shows the mean value of  $E_b$  with the range of uncertainty shown at the left. This binding energy is the same as 0.20 eV/molecule and that is approximately the same energy as has been found for Xe binding to biological molecules in independent experiments.

Our overall conclusion is that the system Xe--n-alkanes is an excellent prototype system for solubility studies. Our study of this system is almost completed and we are now ready to proceed to more complicated systems. These will be discussed in Section III as experiments proposed for the future.



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## B. Diffusion of Inert Gases in Liquids

A second major study that we have made has been diffusion of inert molecules through liquids. In the research which has already been published<sup>3</sup> we studied Xe diffusion through water-sucrose solutions.

The reasons we chose Xe as a diffusing molecule are those described earlier. There are two main reasons for choosing water-sucrose solutions as solvents in these experiments: (1) Sucrose is a common organic molecule whose structure and properties are well known. It is a good compromise molecule, small and simple enough so that one can understand its interactions, yet large and complex enough to serve as a sample of a biologically important molecule. (2) Sucrose is very soluble in water, a solvent which we ultimately want to understand much better. In addition water-sucrose solutions of known viscosity can be readily prepared; this latter is important to us since we want to understand the dependence of the diffusion coefficient on viscosity.

From our work on Xe in water-sucrose solutions we learned that one can use solubility measurements to study interactions in solution. As Figure 1 of Ref. 1 shows, we measured the Ostwald solubility of Xe in solutions ranging from 1.00 volume fraction of water to about 0.45 volume fraction of water. The interesting result shown on Figure 1 of Ref. 1 is that the Ostwald solubility is closely proportional to the volume fraction of water. This suggests the hypothesis that Xe atoms are associated in these solutions with the water molecules. That is, that with respect to Xe solubility the sucrose molecules serve to exclude volume. This is a surprising result since Xe and other nonpolar gases are normally much more soluble in nonpolar liquids than in water.

The main purpose of the work of Ref. 3 was to test the Stokes-Einstein (SE) law, for diffusion of atoms. The SE law is:

$$D = kT/(6 \text{ or } 4)\pi\eta R$$

Eq. (5),



in which  $D$  is the diffusion coefficient,  $k$  is Boltzmann's constant,  $\eta$  is the viscosity of the liquid, and  $R$  is the radius of the diffusing particle. If stick boundary conditions apply then the factor 6 is in the denominator, if slip boundary conditions apply then the factor is 4.

The most important result of the work of Ref. 1 is that the SE law fails to apply for atomic diffusion in this system. Instead of  $D \propto \eta^{-1}$  as predicted by the SE law we observed that  $D \propto \eta^{-0.63 \pm 0.02}$ . This experiment is, we believe, the first such extensive test of the SE law for diffusion of atoms. The results are shown in Fig. 2 of Ref. 1 where the data are given for  $\eta$  ranging from 1 centipoise (distilled water) to 289 cP, this latter corresponds to 68% sucrose by weight in water. The actual relation is:  $D(\text{cm}^2/\text{sec}) = (7.40 \pm 0.39) \times 10^{-7} / \eta^{0.632 \pm 0.017}$  with  $\eta$  in poise. We have discussed the results of this experiment with many scientists and at several meetings. We believe that it is an interesting and important result.

We have also studied diffusion in another system, Xe through the n-alkanes. During that time Dr. John J. Enyeart was a research associate under a Naval Medical Research and Development Command Grant. He was a steady, imaginative and hard working researcher so that the measurements of  $D(\eta)$  for Xe through n-alkanes are essentially complete. He is now a research associate at the University of Rochester. We are making some supplementary measurements; the research will be published soon.

The reason why this system is interesting has been discussed in Section A where the solubility measurements are described. In fact the solubility experiments and the diffusion experiments complement each other. Our diffusion experiments actually give directly the product (Diffusion coefficient)  $\times$  (Ostwald solubility) so that independent measurements of  $L$  are needed in order to obtain  $D$ . Solubility experiments measure an equilibrium property, i.e. the equilibrium distribution of Xe between a gas and liquid phase. Diffusion experiments measure a steady-state transport of molecules from a source to a sink. These measurements then tell us complementary things about the interactions in solution.

C. Papers Published

1. G.L. Pollack, Physical Reviews A 23, 2660-2663 (May 1981). "Atomic Test of the Stokes-Einstein Law: Diffusion and Solubility of Xe".
2. G.L. Pollack, Journal of Chemical Physics 75, 5875-5878 (15 December 1981). "Solubility of Xenon in n-alkanes: n-pentane Through n-hexadecane".
3. G.L. Pollack and J.F. Himm, Journal of Chemical Physics, 77, 3221-3229 (15 September 1982). "Solubility of Xenon in Liquid n-alkanes: Temperature Dependence and Thermodynamic Functions".

#### D. Papers Presented

The following papers have been presented or abstracted on research done under the original NMRDC Contract, since June 1, 1980:

1. "Solubility of Xenon in Liquids", by G.L. Pollack, abstract in Biophysical Journal 33, part 2, 184a (1981). Presented at the Biophysical Society Annual Meeting in Denver, Colorado, February 22-25, 1981.
2. "Solubility of Xenon Gas in Simple Liquids", by G.L. Pollack, Abstract in Bulletin of the American Physical Society 26 322 (1981). Presented at the American Physical Society Meeting in Pheonix, Arizona, March 16-20, 1981.
3. "Solubility and Diffusion of Inert Gases in Liquids", by G.L. Pollack. Presented at VII International Biophysics Congress in Mexico City, Mexico, August 23-28, 1981. Abstract in Proceedings of the Congress.
4. "Solubility and Diffusion of Xenon Gas in Liquid Hydrocarbons", by G.L. Pollack, J. Enyeart, and J.F. Himm. Intended for presentation at the American Physical Society Meeting in Dallas, Texas, March 8-12, 1982. Abstract in Bull. Am. Phys. Soc. 27, 300 (1982).

